

[54] **PRODUCTION OF AROMATIC COMPOUNDS BY OXIDATIVE DEHYDROGENATION**

3,670,042 6/1972 Croce..... 260/680 E
3,670,044 6/1972 Drehman 260/668 D

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[51] Int. Cl.² **C07C 15/14**

[58] Field of Search **260/668 D, 668 R**

[57] **ABSTRACT**

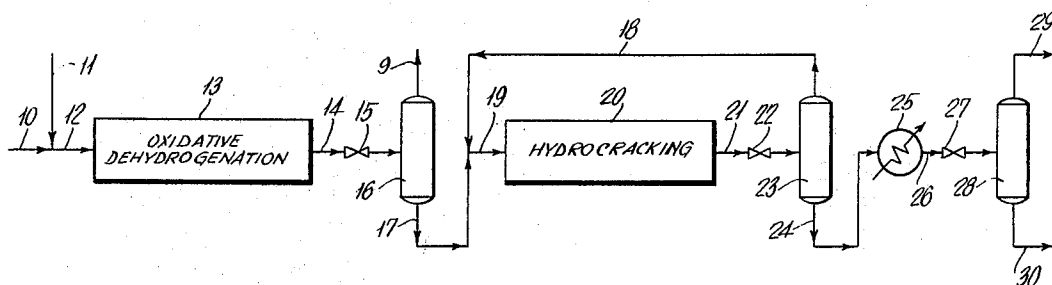
Cyclohexyl benzenes may be selectively oxydehydrogenated to yield aryl aromatics; by-products may be selectively removed by cracking.

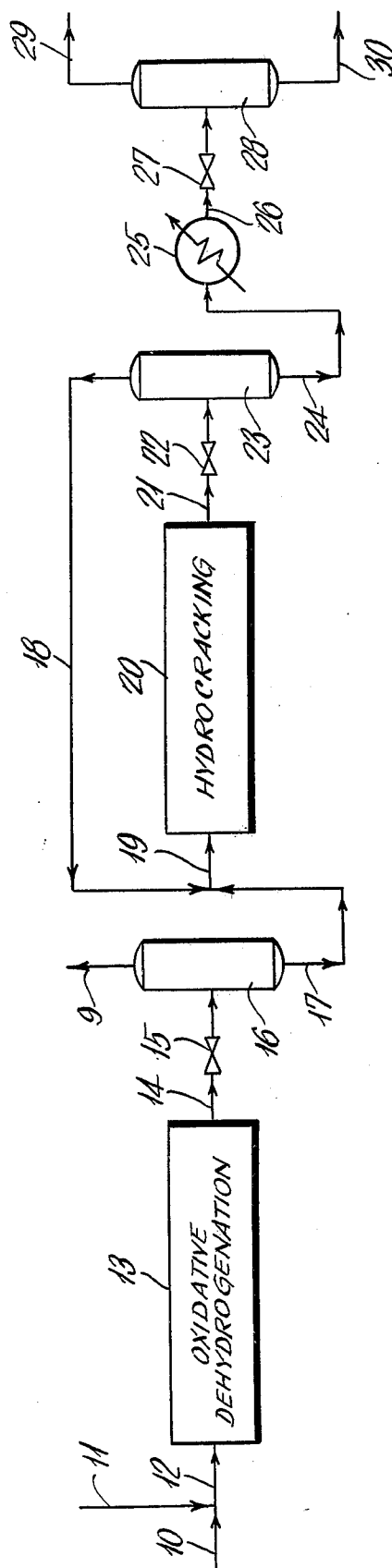
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UNITED STATES PATENTS

3,450,788 6/1969 Kehl et al. 260/680

18 Claims, 1 Drawing Figure





PRODUCTION OF AROMATIC COMPOUNDS BY OXIDATIVE DEHYDROGENATION

BACKGROUND OF THE INVENTION

This invention relates to the preparation of polyphenyls by selective oxidative dehydrogenation of cyclohexyl benzenes. More particularly, this invention relates to the oxidative dehydrogenation of products of hydroalkylation to form desired aromatic hydrocarbons.

As is well known to those skilled in the art, higher molecular weight aromatics, typified by biphenyls and terphenyls, may be difficult to prepare in high purity because of their high boiling point which precludes distillation at reasonable temperatures and pressures. Among the techniques used to recover such materials may be noted vacuum distillation, crystallization, etc. It may be difficult to attain these materials in high purity because many techniques by which they may be recovered, give undesirable yields of by-products or require very severe processing conditions.

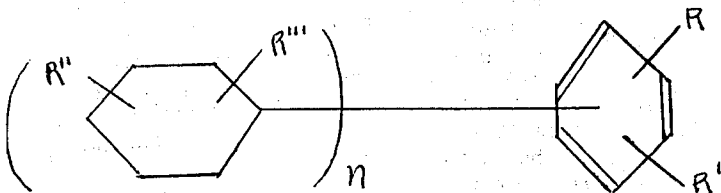
It is an object of this invention to provide a process for preparing selected aromatic hydrocarbons. It is a further object of this invention to provide a process for oxidatively dehydrogenating a cyclohexyl benzene to form aromatic components and to permit recovery of these aromatic components. Other objects will be apparent to those skilled in the art.

STATEMENT OF THE INVENTION

In accordance with certain of its aspects, the novel method of this invention may comprise oxidatively dehydrogenating a naphthenyl benzene in an oxidizing atmosphere at oxidative dehydrogenation conditions in the presence of an oxidative dehydrogenation catalyst thereby forming an oxidatively dehydrogenated stream containing desired aromatic components; and recovering said desired aromatic components.

DESCRIPTION OF THE INVENTION

The charge naphthenylbenzene hydrocarbons which may be treated by the process of this invention may be characterized by the presence of an aromatic ring and at least one naphthenyl cyclohexyl ring. Typically the charge cyclohexyl benzene hydrocarbons may be represented by the formula:



In the above formula n may be an integer 1-4 preferably 1 or 2. R , R' , R'' , and R''' may be hydrogen or lower alkyl; when R , R' , R'' , or R''' is lower alkyl, it may preferably be methyl or ethyl.

In a preferred embodiment, the naphthenyl cyclohexyl group and the aromatic benzene ring may contain the same number of carbon atoms and may possess the same configuration. For example, if the naphthenyl moiety is cyclohexyl, the aromatic moiety may be phenyl; if the naphthenyl moiety is methylcyclohexyl, the aromatic moiety may be tolyl; etc.

Typical examples include, where $n = 1$, cyclohexyl

benzene, methylcyclohexyl toluenes (12 isomers), (ethylcyclohexyl) ethyl benzenes, (dimethylcyclohexyl) xylenes, etc.;

Where $n = 2$

- 5 para-dicyclohexyl benzene
- meta-dicyclohexyl benzene
- ortho-dicyclohexyl benzene
- dicyclohexyl toluenes
- di(ethylcyclohexyl) ethyl benzenes
- 10 (methylcyclohexyl) cyclohexyl benzene
- di(methylcyclohexyl) toluenes
- di(dimethylcyclohexyl) xylenes

Where $n = 3$

- 1,3,5-tricyclohexyl benzene
- 15 1,2,4-tricyclohexyl benzene
- tri(methylcyclohexyl) toluenes
- tri(ethylcyclohexyl) ethyl benzenes

Mixtures of (substituted cyclohexyl) substituted benzenes can be formed by hydroalkylating substituted benzene. For example, the hydroalkylation of benzene results in a mixture that contains (aside from unreacted benzene) cyclohexyl benzene, dicyclohexyl benzenes (para, meta- and ortho isomers), and tricyclohexyl benzenes.

The hydroalkylation of toluene forms a mixture containing (methylcyclohexyl) toluenes, di(methylcyclohexyl) toluenes, and tri(methylcyclohexyl) toluenes.

In hydroalkylating xylenes, (dimethylcyclohexyl) xylenes and di(dimethylcyclohexyl) xylenes and tri(dimethylcyclohexyl) xylenes are formed.

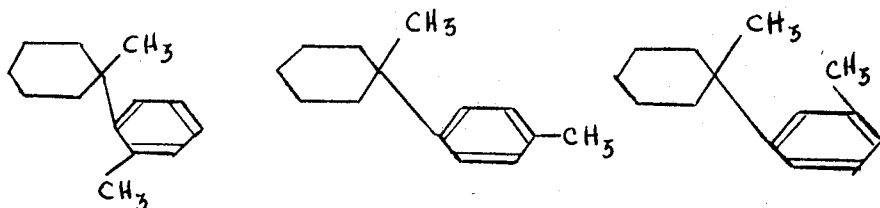
When mixtures of aromatics, such as either benzene and toluene or C_6-C_8 aromatics are hydroalkylated, additional compounds may be formed such as:

- 35 cyclohexyl toluenes
- (methylcyclohexyl) benzenes
- methylcyclohexyl cyclohexyl toluenes
- methylcyclohexyl cyclohexyl benzenes
- 40 di(methylcyclohexyl) benzenes
- dicyclohexyl toluenes
- cyclohexyl xylenes
- cyclohexyl ethyl benzenes
- methylcyclohexyl xylenes
- 45 (ethylcyclohexyl) xylenes
- di(ethylcyclohexyl) xylenes
- di(dimethylcyclohexyl) ethyl benzenes

- (ethylcyclohexyl) (dimethylcyclohexyl) ethyl benzene
- 60 (ethylcyclohexyl) (dimethylcyclohexyl) xylenes
- (ethylcyclohexyl) cyclohexyl toluenes
- (ethylcyclohexyl) cyclohexyl benzenes
- (ethylcyclohexyl) cyclohexyl xylenes

While a large number of isomers of (substituted cyclohexyl) substituted benzenes can be formed by hydroalkylation, many of these isomers occur, if at all, in very low concentration. In particular, the formation of isomers where an alkyl group is substituted on the same carbon that bonds the cyclohexyl group to the benzene ring, is sterically not favored during hy-

droalkylation. For example, when hydroalkylating toluene, the formation of the following isomers is not favored because of steric factors:



It is a feature of the process of this invention that such compounds as these are not preferred charge materials.

Similarly it is understood that when the (dimethylcyclohexyl) benzenes, (dimethylcyclohexyl) toluenes, and (dimethylcyclohexyl) xylenes are formed by hydroalkylating an aromatic containing xylenes, the two methyl groups on the cyclohexyl ring are not attached to the same carbon. That is, the carbon in the cyclohexyl ring to which a methyl group is attached must also have a hydrogen substituent to permit the facile dehydrogenation of the cyclohexyl ring.

It is a feature of the process of this invention that the hydroalkylating reaction does not favor the formation of such undesirable compounds as described above. Thus, the hydroalkylating reaction is ideally suited for the preparation of the feed materials for the process of this invention.

It is to be appreciated that other compounds can be formed in minor amounts during the hydroalkylation. Some, such as bicyclohexyl or other substituted bicyclohexyls, are suitable feed material for the subject process. However, most by-products of the reaction do not contribute substantially to the desired products.

For example, during the hydroalkylation of benzene, (methylcyclopentyl) benzenes are formed which possess physical properties similar to cyclohexyl benzene and hence are difficult to separate from the cyclohexyl benzene. Likewise, the dicyclohexyl benzene distillate fraction contains impurities such as (methylcyclopentyl) cyclohexyl benzenes. While the dicyclohexyl benzenes are preferred materials for forming terphenyls, the impurities do not generate terphenyls, although some biphenyls can be formed if the methylcyclopentyl group can be cracked off.

In addition, when hydroalkylating benzene, cyclohexane and methylcyclopentane are also formed.

Similar cyclopentyl impurities are formed in hydroalkylating toluene, xylenes, and ethyl benzenes or mixtures thereof with or without benzene.

In addition, naphthenes corresponding to the feed aromatic are also formed during hydroalkylation. Thus, for example, cyclohexane and methylcyclopentane are formed during the hydroalkylation of benzene. Likewise, methylcyclohexane and dimethylcyclopentanes are generated during the hydroalkylation of toluene; dimethylcyclohexanes and trimethylcyclopentanes in hydroalkylation of xylenes; and ethylcyclohexane and methylethylcyclopentanes in hydroalkylation of ethylbenzene.

These saturated naphthenes are inert under hydroalkylation conditions. That is, cyclohexane does not react with benzene to make cyclohexyl benzene. It has been heretofore necessary then to eventually separate these naphthenes from the charge aromatic and then

dispose of them.

It is a feature of the process of this invention that these saturated naphthenes may be included in the

(substituted cyclohexyl) substituted benzene feed either for dehydrogenation back to the parent aromatic as in the case of the cyclohexane derivatives, or for cracking to light product as in the case of the cyclopentane derivatives. In either event, their inclusion in the feed to the process of the invention together with non-hydroalkylated aromatic, e.g. benzene, toluene, xylenes, or ethylbenzene, can provide a means of reconcentrating or purifying the feed aromatic prior to recycling the aromatic back to the hydroalkylation reactor.

The particular composition of the feed to dehydrogenation will be dictated by the products desired. For example, if para-terphenyl is desired, then the feed should contain para-dicyclohexyl benzene such as may be provided either as a mixture or with further purification (e.g. as by the processes disclosed in U.S. Pat. Nos. 3,784,617 or 3,784,618 or 3,784,619). Likewise, to make meta-terphenyl, the feed should contain meta-dicyclohexyl benzene.

Biphenyl and terphenyls may be made simultaneously by employing as feedstock a mixture containing cyclohexyl benzene and dicyclohexyl benzenes.

The effluent from a hydroalkylation unit may be used, with or without further separation depending on the polyphenyl products desired. The total hydroalkylation effluent (hydrocarbons) may be heated up, and passed to the oxidative dehydrogenation operation.

In one preferred embodiment, there may be admitted with the charge at least a portion of the recycled product stream either before or after the latter is purified.

In practice of the process of this invention, the charge cyclohexyl benzene may be oxidatively dehydrogenated, in an oxidizing atmosphere at oxidative dehydrogenation conditions in the presence of oxidative dehydrogenation catalyst, which may preferably be a non-acidic catalyst, thereby forming an oxidatively dehydrogenated stream containing (i) desired aromatic components and (ii) undesired components having a naphthenyl-aromatic bond.

The oxidative atmosphere in which the process of this invention may be carried out may contain air, oxygen, oxygen-enriched air, etc. Typically, the atmosphere may contain 0.5-20 moles, preferably 1-3 moles, say 1.75 moles of oxygen per mole of charge cyclohexyl rings. For example, for a charge containing only cyclohexyl benzenes, the preferred molar ratio of molecular oxygen to cyclohexyl benzene may be 1-3:1, preferably 2:1. For dicyclohexyl benzenes, the corresponding ratio would preferably be 2-6:1, preferably about 4:1. The total amount of oxygen utilized may be introduced into the gaseous mixture entering the catalytic zone; alternatively, it may be desirable to add the oxygen in increments in order to assist in controlling the reaction. The oxygen may be added directly, or it may be premixed, for example, with a diluent or with

steam.

Oxidative dehydrogenation is carried out at oxidative dehydrogenating conditions including a temperature of 400°F–1100°F, preferably 550°F–900°F, and at a total pressure of 4–300 psia and preferably less than about 75 psia. Satisfactory results may be obtained at atmospheric pressure.

The initial partial pressure of the hydrocarbon to be dehydrogenated together with the oxygen will preferably be equivalent to less than about 25% of the total pressure. Partial pressure may be maintained by the use of diluents such as nitrogen, helium, or other gases. Preferably the reaction mixture contains 2–50, typically 5–30 moles steam per mole of hydrocarbon to be dehydrogenated.

Reaction may be carried out in the presence of a supported catalyst where the support preferably has a surface area of less than about 50 square meters per gram. Catalyst supports which may be employed as preferred nonacidic supports include neutral and basic supports. Typically such supports contain basic moieties in their structure (including groups adsorbed thereon), or they may be neutral. In preferred embodiments, they may be pretreated with aqueous caustic (e.g. sodium hydroxide or more preferably potassium hydroxide) and calcined. Typical of such supports are low area supports including alpha-alumina, kieselguhr, spinels (MgAl_2O_4), etc. These catalyst supports may contain alkali or alkaline earth elements to serve as selectivity moderators. Typical of these are BaO , K_2O , or Na_2O present in amount up to about 2% or Li_2O present in amount up to about 1%.

There may be deposited on and within the support (when the catalyst is the preferred supported catalyst) at least one metal selected from the group consisting of rhenium Re, a Group VI-B metal, a Group I-B metal, a Group VIII metal, uranium U, bismuth Bi, and antimony Sb. When the metal is a Group VI-B metal, it may be chromium Cr, molybdenum Mo, or tungsten W. When the metal is a Group I-B metal, it may be copper Cu, or silver Ag.

A typical supported catalyst may be prepared by impregnating 1% palladium onto an alpha-alumina containing 0.4% sodium and having a surface area of 5 square meters per gram. The catalyst may be in pellet form for fixed-bed operation, or in powder form for fluidized-bed operation.

Catalysts containing noble metals should be used at lower temperatures of typically 400°F–700°F; oxide-type catalysts such as ferrites, copper chromite, q.v. infra, etc., may be used at higher temperatures — typically up to about 1,100°F, e.g. 700°F–1,100°F.

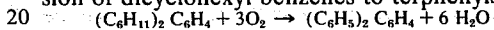
Reaction may alternatively be carried out in the presence of a non-supported catalyst. Typical of non-supported catalysts which may be employed are: composite oxide catalysts such as copper chromite; or ferrites, which are magnetic oxides containing ferric iron as a major metallic component, including magnetite, Fe_3O_4 , magnesioferrite MgFe_2O_4 , cobalt ferrite, and mixed ferrites including those of iron, magnesium, cobalt, nickel, or zinc, e.g. nickel-zinc ferrite.

A typical ferrite catalyst, cobalt ferrite, may be formed by dissolving 72.8 g of cobaltous nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and 175 g of ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ in 1 liter of distilled water. This solution is slowly added, with stirring, to a solution containing 100 g of sodium hydroxide in 1 liter of distilled water. A coprecipitate of cobaltous and ferric hydroxides is obtained

which is filtered and washed with distilled water until it is neutral. The mixture is dried at 220°F and then heated to 1,700°F for 2 hours. A magnetic black solid cobalt ferrite is obtained.

In accordance with practice of the process of this invention, oxidative dehydrogenation may be effected to convert the naphthenyl aromatic cyclohexyl benzene to a desired aromatic component in which the product naphthenyl moiety contains less hydrogen than does the charge naphthenyl moiety. In the preferred embodiment, the charge naphthenyl moiety is selectively converted to high yields of aromatic moiety — and in typical operation, the charge naphthenyl cyclohexyl moiety may be selectively converted to aromatic phenyl moieties in conversion of 30%–100%, preferably 50%–100%, say 70%.

During oxidative dehydrogenation, the following typical reaction may occur in the case of the conversion of dicyclohexyl benzenes to terphenyls:



The product stream may typically contain desired aromatic components typically containing less hydrogen than does the charge component and thus possessing a higher degree of unsaturation. In the preferred embodiment, the cyclic moieties in the product will contain a higher degree of aromatic unsaturation. In the case of oxidative dehydrogenation of, e.g., cyclohexyl benzene, the product stream will contain the desired phenyl benzene (i.e., biphenyl). In the case of oxidative dehydrogenation of dicyclohexyl benzene the product stream will contain the desired diphenyl benzene (i.e. terphenyl) — the latter compound is particularly useful as a heat transfer medium.

The product stream will also contain undesired naphthenyl aromatic cyclohexyl benzene components. In the case of oxidative dehydrogenation of cyclohexyl benzene, the product stream may contain undesired unconverted cyclohexyl benzene plus undesired cyclohexenyl benzene and cyclohexadienyl benzene as well as other impurities such as (methylcyclopentyl) benzene present in the cyclohexyl benzene feed. In the case of charge dicyclohexyl benzene, the undesired components in the product stream may contain cyclohexyl, phenyl benzene; dicyclohexenyl benzene; cyclohexyl, cyclohexenyl benzene plus other cyclopentyl derivatives that are present in the dicyclohexyl benzene feed, etc.

It is a feature of the process of this invention that unexpectedly the reaction conditions which are conducive to oxidative dehydrogenation of the charge naphthenyl aromatic, cyclohexyl benzene hydrocarbon desirably give little or no cracking of the naphthene-aromatic bond. Typically less than 30 wt. percent of the charge is cracked by rupture of this bond.

When dehydrogenating a crude stream recovered, for example, from the hydroalkylation of benzene which may contain a mixture including benzene, cyclohexane, cyclohexyl benzene, methylcyclopentyl benzene, dicyclohexyl benzenes, (methylcyclopentyl) cyclohexyl benzene, etc., the dehydrogenation product mixture may contain:

benzene
methylcyclopentane
cyclohexane
biphenyl
methylcyclopentyl benzenes
methylcyclopentenyl benzenes
methylcyclopentadienyl benzenes

trace amounts of cyclohexyl benzene
terphenyls
cyclohexylphenyl benzenes
(methylcyclopentyl), phenyl benzenes
dicyclohexyl benzenes

Biphenyl and the terphenyls present may be recovered from the above mixture by fractionation and then purified. Biphenyl and terphenyls may be recovered by crystallization of these distillate cuts.

The high boiling residues (higher boiling than benzene) from these recovery steps may in part be recycled to the dehydrogenation reactor to effect further conversion of species such as unreacted cyclohexyl benzene and dicyclohexyl benzene. A portion, however, should be drawn off and discarded or preferably cracked at high temperatures to recover benzene and biphenyl.

With mixtures of (substituted cyclohexyl) substituted benzene (such as formed by hydroalkylating toluene, xylene or ethylbenzene) are dehydrogenated, it will be appreciated that the number of possible bi(substituted phenyls) and ter(substituted phenyls) products is large; and the mixed biphenyls or mixed ter(substituted phenyls) can not be easily separated from unreacted species of similar boiling range by means of crystallization techniques alone.

It is a feature of this invention that the product of oxidative dehydrogenation containing these desired poly(substituted phenyls) can be purified of naphthenyl derivatives by cracking the naphthenyl groups.

In practice of the process of this invention, the oxidatively dehydrogenated stream as withdrawn from oxidative dehydrogenation (and, in the preferred embodiment, with no intermediate treatment) may be cracked (e.g. hydrocracked) at cracking conditions. When this stream is cracked, it may be cracked at 500°F–1,100°F, preferably 700°F–1,100°F, say 875°F. When the stream is hydrocracked, this may be effected at 500°F–900°F, preferably 600°F–800°F, say 700°F at 0–2,000 psig, preferably 200–1,000 psig, say 750 psig.

Hydrocracking may be carried out in liquid phase over an acidic catalyst containing at least one metal selected from the group consisting of rhenium, Group VI-B metals, and Group VIII metals. The catalyst metals may preferably be in a sulfided form, and preferably be supported on an acidic support such as alumina, silicaalumina, acid zeolites, etc. The catalyst may be prepared by impregnating an acidic catalyst (such as (i) alumina, preferably fluorided with 1–10%, say 3–6% fluoride, with ammonium fluoride and then calcined or (ii) silicaalumina, or (iii) magnesium, calcium or rare earthexchanged zeolite with nickel and molybdenum. When cracking is not done in the presence of added hydrogen, preferred catalyst may be silica-alumina; or magnesium, calcium or rare earth exchanged zeolite at 700°–1,100°F.

Preferably, a light aromatic stock such as one containing benzene or toluene may be included in the feedstock to the cracking reaction to assist in removal of the polyphenyl product; such a diluent may help to wash off the strongly sorbed biphenyl or ter(substituted phenyl(s)) from the catalyst.

It is a feature of the process of this invention that mild cracking will rupture the naphthene-to-aromatic bond(s) in the undesired components without rupturing the aromatic-aromatic bonds in the desired components. In the case of charge dicyclohexyl benzenes which have been oxidatively dehydrogenated to desired

terphenyl and which contain, e.g., unconverted dicyclohexyl benzenes, the latter are cracked to a lower boiling fraction containing benzene, toluene, and light olefins.

This difference in boiling point makes it readily possible to separate the desired products from the undesired products as by distillation or by flashing in the case of poly(substituted phenyl) compounds. Such a separation is not readily or conveniently possible in the case of the uncracked stream because the boiling ranges of the desired poly(substituted phenyl) compounds and those of the undesired naphthenyl aromatics may overlap.

In the case of the charge dicyclohexyl benzenes, the product (ex hydrogen) leaving cracking or hydrocracking may typically contain 60 parts of terphenyls, 30 parts of biphenyls, 5 parts of benzene, 3 parts of toluene, 2 parts of ethylbenzene, and 15 parts of light hydrocarbons including olefins, C₁ to C₄ paraffins, etc.

In practice of the process of this invention, the cracked product may be passed to separation. Although this may be carried out in a distillation column, it is a feature of this invention that desired aromatic components may be readily separated from the undesired lower boiling products in the stream recovered from cracking, by flashing off light components; and the e.g. biphenyls and terphenyls may be separated by distillation.

This process may be useful to prepare a wide variety of aromatics products (in good purity and yield) which could only be attained less conveniently, if at all, by other possible processes, e.g., ditolyls or tolyl toluenes typified by para(para-tolyl)-toluene; terphenyl; 1,3,5-triphenyl benzene; meta-tolyl benzene; etc.

It is particularly unexpected that one should be able to selectively operate in manner (a) to dehydrogenate without cracking, thereafter (b) to be able to selectively crack the undesired components without destruction of the desired components, and (c) to then easily separate the desired components.

Practice of the process of this invention will be apparent to those skilled in the art from inspection of the following wherein, as elsewhere in this application, all parts are parts by weight unless otherwise stated.

EXAMPLE I

a. In this example which represents a preferred embodiment of this invention, a copper chromite catalyst containing 2% barium oxide is prepared from

- i. 4 liters of aqueous solution containing 591 g of copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1,600 g of chromic nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 8 g of barium nitrate $\text{Ba}(\text{NO}_3)_2$; and
- ii. 4 liters of 1.3 molar ammonium hydroxide.

The two solutions are added simultaneously at the same rate, over a 1-hour period, to a well-stirred vessel containing one liter of acetone. After the addition is complete, the mixture is stirred for an additional hour, filtered, and washed with 2 volumes of water.

The precipitate is dried for 4 hours at 200°F, calcined to 700°F (the temperature being increased at a rate of 100°F/hour) and held at 700°F for 2 hours. The calcined product is powdered and mixed with 4% graphite binder, pelleted and calcined in air at 1,100°F for 2 hours.

b. Oxidative dehydrogenating may be carried out by passing cyclohexyl benzenes (236 g/hr) and 78 g/hr of benzene at 800°F and 0 psig into contact with 50 cc of

the catalyst. 33 liters of air and 53 cc of water are also admitted. The mole ratio of steam:oxygen:cyclohexyl benzene is 20:2:1.

The product from oxidative dehydrogenation may contain 25 g of unconverted cyclohexyl benzenes, 13 g of biphenyl, and 5 g of other naphthenyl aromatics dissolved in benzene.

c. The product recovered from oxidative dehydrogenation may be cracked over an acidic silica-alumina cracking catalyst at 800°F and 0 psig to yield a product containing 12 parts of desired diphenyl and less than 0.2 g of other aromatic materials which boil near biphenyl.

Cracked effluent may be withdrawn from cracking and flashed thereby separating 30 parts of overhead containing components boiling at temperature below the boiling of diphenyl. Bottoms recovered in amount of 12 g includes desired diphenyl.

Results comparable to those achieved in Example I may be obtained by the following:

EXAMPLE II

The process of Example I may be carried out except that the oxidative dehydrogenation catalyst may contain unsupported copper chromite (a non-acidic catalyst) containing 1 mole of Cu_2O per 1 mole of Cr_2O_3 , and using as charge hydrocarbon a crude dicyclohexyl benzene containing 30% para-isomer and 65% ortho- and meta-isomer and 5% impurities — oxidatively dehydrogenated at 800°F and 15 psig and LHSV of 3.

EXAMPLE III

An impure "toluene dimer" stock was prepared from toluene (which had been dried over silica gel) by hydroalkylation. The catalyst contained (i) 78% amorphous silica-alumina matrix within which was dispersed (ii) 22% of hydrogen Y zeolite containing 4% nickel. Hydroalkylation was carried out at inlet temperature of 320°F, exit temperature of 405°F, pressure of 473 psig, 3 LHSV, and complete consumption of hydrogen admitted (1.8 parts per 100 parts of toluene). The product contained 0.57% dimethylcyclopentane, 13.16% methylcyclohexane, 18.0% "toluene dimers", i.e. methylcyclohexyl toluenes, 0.62% "toluene trimers", i.e. di(methylcyclohexyl) toluenes, and the remainder, toluene.

The "toluene dimers" contain methylcyclohexyl toluenes and dimethylcyclopentyl toluenes. The "toluene trimers" contain di(methylcyclohexyl) toluenes and other dinaphthenyl toluenes.

The "toluene dimers" may be recovered by fractionating to recover the material boiling at 500°F–600°F. These dimers may be oxidatively dehydrogenated over a catalyst prepared by impregnating ammonium molybdate solution onto alumina pellets containing 1% sodium. The impregnated catalyst, containing 14% molybdenum, is dried for 5 hours at 220°F and calcined for 4 hours at 930°F in a stream of hydrogen at atmospheric pressure.

The "toluene dimer" may then be introduced into an oxidative dehydrogenation operation at LHSV of 0.5 at 900°F and 20 psig. Charge also includes benzene diluent (in amount of 30% of the "toluene dimer"). Air and water are admitted to give a molar ratio of steam:oxygen:toluene dimer of 20:2:1.

EXAMPLE IV

Practice of the process of this invention may be apparent by reference to the drawing which schematically shows a flow sheet according to which the process may be carried out.

In the drawing, there may be admitted through line 10, a dicyclohexyl benzene charge in amount of 100 parts containing 30 parts of para-isomer and 65 parts of ortho- and meta-isomers, and 5 parts of dinaphthenyl benzene boiling in the dicyclohexyl benzene range. 20 moles of steam and 2 moles of oxygen (as air) per mole of charge dicyclohexyl benzene are shown as being admitted through line 11; and the mixture admitted through line 12 to dehydrogenation operation 13 at LHSV of 3. Catalyst in operation 13 is copper chromite containing barium prepared as in Example I supra. Dehydrogenation is effected at inlet temperature of 800°F and pressure of 0 psig.

Effluent is preferably passed through line 14, and valve 15 to separation 16. By-products such as water, nitrogen, etc., are separated through line 9.

Dehydrogenated product in line 17 may be mixed with hydrogen (the hydrogen being admitted through line 18) and the mixture passed through line 19 to hydrocracking operation 20. The catalyst in hydrocracking operation 20 may be acidic silica-alumina. Inlet temperature in line 19 is 850°F at 0 psig.

Effluent from hydrocracking may be passed through line 21 and valve 22 to separation operation 23 wherein hydrogen may be separated and recycled to the charge to hydrocracking. The effluent (ex hydrogen) may contain terphenyl, biphenyl, light aromatics added as diluent (e.g. benzene), light hydrocarbons (e.g. cyclohexane), etc.

Hydrocracked product in separation operation 23 may be withdrawn through line 24, heated in heat exchanger 25, passed through line 26 and valve 27, and flashed in flash drum 28.

Overhead removed through line 29 may contain the light components; and the desired product terphenyl may be recovered in amount of 55 parts of substantially pure product through line 30.

It will be apparent to those skilled in the art that the drawing is schematic; and that various pumps, heat exchangers, collection vessels, etc., are not specifically shown.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of this invention.

I claim:

1. The method which comprises oxidatively dehydrogenating a naphthenyl benzene in an oxidative atmosphere at oxidative dehydrogenation conditions in the presence of oxidative dehydrogenation catalyst thereby forming an oxidatively dehydrogenated stream containing desired aromatic components; and recovering said desired aromatic components.

2. The method claimed in claim 1 wherein said oxidative dehydrogenation is carried out at 400°F–1,100°F.

3. The method claimed in claim 1 wherein said catalyst is a supported catalyst containing at least one metal selected from the group consisting of rhenium, Group VI B metals, Group I B metals, Group VIII metals uranium, bismuth, and antimony on a low surface area

11

support having a surface area less than about 50 square meters per gram.

4. The method claimed in claim 1 wherein said catalyst includes a Group VIII metal on non-acid support.

5. The method claimed in claim 1 wherein said catalyst includes an unsupported catalyst selected from the group consisting of copper chromite and ferrites.

6. The method claimed in claim 1 wherein said catalyst includes copper chromite containing barium.

7. The method claimed in claim 1 wherein said naphthenyl benzene is cyclohexyl benzene se.

8. The method claimed in claim 7 wherein said naphthenyl benzene is a dicyclohexyl benzene.

9. The method which comprises oxidatively dehydrogenating a dicyclohexyl benzene in an oxidative atmosphere at oxidative dehydrogenation conditions including pressure of 4-300 psia and temperature of 700°F-1100°F in the presence of an oxidative dehydrogenation catalyst containing a copper chromite thereby forming an oxidatively dehydrogenated stream containing terphenyl; and recovering said terphenyl.

10. The method claimed in claim 9 wherein said temperature is 750°F-1000°F.

11. The method which comprises oxidatively dehydrogenating a naphthenyl benzene in an oxidative atmosphere at oxidative dehydrogenation conditions in the presence of oxidative dehydrogenation catalyst thereby forming an oxidatively dehydrogenated stream containing (i) desired aromatic components and (ii) undesired components having a cyclohexyl-aromatic bond;

cracking said oxidatively dehydrogenated stream at cracking conditions thereby rupturing at least a portion of said cyclohexyl-aromatic bonds and forming lower boiling products;

separating said lower boiling products; and recovering said desired aromatic components.

12. The method claimed in claim 11 wherein said cracking is hydrocracking.

13. The method claimed in claim 11 wherein said cracking is carried out in the presence of acidic catalyst at 700°-1100°F.

14. The method claimed in claim 11 wherein said cracking is carried out in the presence of a Group VIII metal sulfide on magnesium, calcium or rare earth exchanged zeolite.

12

15. The method claimed in claim 11 wherein said cracking is hydrocracking carried out at 500°F-900°F.

16. The method claimed in claim 11 wherein said naphthenyl benzene contains at least one component selected from the group consisting of cyclohexyl benzenes and dicyclohexyl benzenes.

17. The method which comprises oxidatively dehydrogenating a cyclohexyl benzene in an oxidative atmosphere at oxidative dehydrogenation conditions including pressure of 4-300 psia and temperature of 550°F-900°F in the presence of oxidative dehydrogenation catalyst containing at least one metal selected from rhenium, Group VI B metals, Group I B metals, Group VIII metals uranium, bismuth, and antimony thereby forming an oxidatively dehydrogenated stream containing (i) desired aromatic components and (ii) undesired components having a cyclohexylaromatic bond;

hydrocracking said oxidatively dehydrogenated steam at cracking conditions including temperature of 500°F-900°F and 0-2000 psig thereby rupturing at least a portion of said cyclohexyl-aromatic bonds and forming lower boiling products;

separating said lower boiling products; and recovering said desired aromatic components.

18. The method which comprises oxidatively dehydrogenating a charge stream containing dicyclohexyl benzene in an oxidative atmosphere at oxidative dehydrogenation conditions including pressure of 4-300 psia and temperature of 700°F-1100°F in the presence of a oxidative dehydrogenation catalyst including copper chromite containing barium thereby forming an oxidatively dehydrogenated stream containing (i) desired terphenyl and (ii) undesired components having a cyclohexyl-aromatic bond;

hydrocracking said oxidatively dehydrogenated stream at cracking conditions including temperature of 500°F-900°F and 0-2000 psig in the presence of an acidic catalyst thereby rupturing at least a portion of said cyclohexyl-aromatic bonds and forming lower boiling products;

separating said lower boiling products; and recovering said desired terphenyl.

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